A NEW APPROACH FOR SERVICE LIFE EVALUATION
OF GUN PROPELLANT

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BACKGROUND

The ability to predict how long gun propellant will remain serviceable (i.e., safe and functional) has been a concern of the US Navy for decades. The initial ordnance service life program began in 1944. Historically, service life programs have provided very limited extensions for service life of gun propellant. One of the primary reasons for this short coming is that gun propellant contains nitrate esters (nitrocellulose, nitroglycerin, or both). Nitrate esters are by their very nature, unstable. During the course of storage, gun propellant slowly and spontaneously releases nitrogen oxides (a red color fume). Stabilizer is added to the propellant at the time of manufacturing to serve as a "trap" for the oxides. Without the stabilizer, or when the stabilizer content is low, the liberated nitrogen oxides can catalyze the decomposition of the original nitrate esters. This reaction is exothermic and can eventually lead to autocatalysis (self-ignition) of the gun propellant. Most Naval gun propellants are subjected to periodic fume tests throughout their lifetime to hopefully assure that they remain in a stable condition safe for storage and handling.

All objective studies of fuming process have indicated that the test is simply a pass / fail procedure with no quantifiable content. A review of an incident which occurred in 1976 at ARDEC, revealed that the red fume produced in the test could fade in a few days. At some time after the red fume fading, many types of propellant could self-ignite. Therefore, it was concluded that the time-to-fume test is clearly not an accurate and safe predictive test method.

Today the routine use of more precise technology such as the HPLC (High Performance Liquid Chromatography) has greatly enhanced our understanding of the effective stabilizer contents remained in the propellant. While this HPLC data is useful for assessment of the current stability condition, it does not predict the future safe storage life of the propellant.

The NATO test method has improved the capability of future shelf life prediction by combining the HPLC analysis of the stabilizer levels before and after accelerated aging test (65.5°C for 90 or 120 days). The NATO test method is based on a kinetic model established by the observed rate of stabilizer depletion. However, the complexity of the solid state kinetics may make it very difficult to derive a rate law truly representing the propellant degradation process.

Since 1988, NSWC Crane Division has been involved in developing a method, which can determine the safe storage life of various energetic compositions. The genesis of this method is the Heat Flow calorimeter. When used in conjunction with the HPLC, the combined HPLC/Heat Flow calorimetry can provide a very accurate time frame for the remaining stable life of the

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propellant.

This paper will deal with a new predictive gun propellant service life program which provides the Fleet a higher level of confidence in their ammunition and also provides the Ammo Managers with the decision tools they need to more effectively manage their assets.

INTRODUCTION

As previously stated, most of the work done in support of gun propellant service life was in one way or the other, directly related to stabilizer depletion.   While it is self-evident that stabilizer is very important, it is not the only attribute which can effect both the safety and serviceability of our ammunition stockpile.   It is very possible for a propellant to have ample stabilizer and also have unsafe or unsatisfactory performance. In other words, the stabilizer level does not provide all of the information that the Fleet and Ammo Manager need.

It has been apparent to most surveillance scientists that the key to improving all service life programs is the ability to artificially age gun propellant to predetermined ages.   This would allow for performance testing of aged assets and the establishment of how well ammunition will work in the future.   However, any aging process developed would have to be highly accurate, relatively quick, and reasonably economical if it is to be successful. There have been a number of attempts to conduct accelerated aging programs in the past, however, these experienced a number of problems.   Most of these programs would attempt to accelerate the aging process by exposing the test item to relatively long term, moderately elevated temperature conditions. The guideline for most of these programs was to accomplish a two to one time compression ratio, i.e., one year of storage would equal two years of in-service life.   While these programs had a modest level of success in predicting what the eventual life limiting defect would be for large items like rocket motors, the cost was high and the ability to provide Logistic Managers with long term service life predictions was very limited.

NEW PROGRAM GENESIS

With the advent of Heat Flow Calorimetry a number of barriers have been overcome.   This new tool has provided that missing essential element that measures the rate of heat reaction at real world temperature ranges.   The data generated lays the foundation of the first truly accurate long range accelerated aging program. The basic flow of this new service life program, the Predictive Surveillance program is shown in Figure 1.

While it is valid to say that the Heat Flow Calorimeter is the genesis of the Predictive Surveillance program, it is also true that it is only one element of the program.   All too often when new technologies become available there is a tendency to use it to the exclusion of all other techniques or processes.   The strength of the Predictive Surveillance program is that it does not see the heat flow calorimeter as a panacea, but rather, it is a very powerful starting point.   It is only through a wide ranging and comprehensive evaluation program that true safety, reliability and service life of any energetic item can be identified.

Figure 1
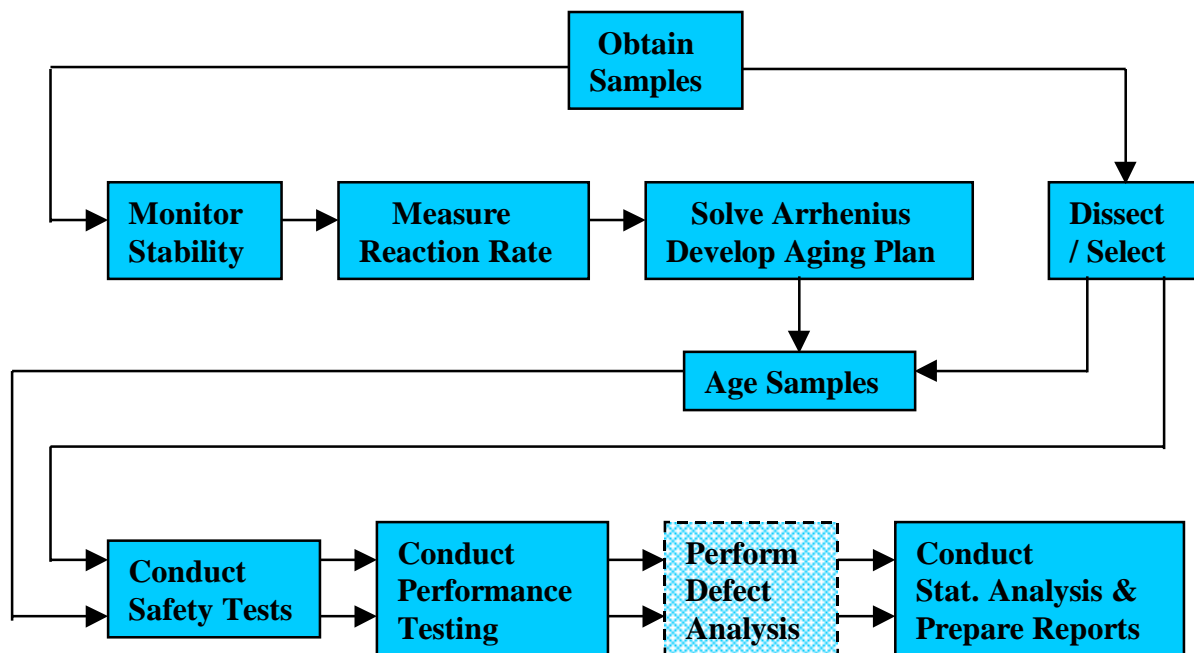
THE PREDICTIVE PROCESS

The processes of the Predictive Surveillance program are more easily understood by analyzing its three fundamental stages as separate elements.   These elements are:

        a. the Kinetics study
        b. the aging program and
        c. the safety / performance test element.

The Kinetic Study Element - The goal of this program element is to gather data on the long term chemical stability, the total available energy, the heat of reaction at various temperatures, and a profile of how the material under test will change chemically as it ages.   There are three primary tools used to accomplish this sub-program: 1) the Differential Scanning Calorimetry (DSC), 2) the HPLC, and 3) the Heat Flow Calorimeter

        DSC - In the Predictive Surveillance program the DSC is used for two important functions. The first use of this tool is to act as a screening agent.   If the material under investigation is already at the point of chemical instability, the DSC will detect this and the kinetics work can be terminated before it becomes a hazard to any individuals or equipment. The second function of this equipment is to provide a measurement of the

total energy available per unit of mass.   This reading is obtained by Iso-DSC measurement and is used in conjunction with other data generated by the Heat Flow calorimeters to determine the percent of degradation.

HPLC - As with all applications of the HPLC, the primary function of this analytical tool is to determine the chemical constituents of the material under investigation.   In the case of Predictive Surveillance, this process is used in conjunction with the microcalorimeter. A relatively large sample of the material under test is placed in an oven at the same temperature as the highest microcalorimeter sample.   Small portions of this material are then periodically removed from the oven and run through the HPLC.   This provides a running history of how the material under investigation changes chemically as it undergoes aging.   Clearly, this data also provides a more complete understanding of the aging process and thus helps to determine causes of safety or performance shifts.

Heat Flow Calorimeter - The calorimeter is obviously the new player in the Kinetics arena. The Predictive Surveillance program uses this new technology for a number of reasons; the results are very reproducible, highly accurate, obtained at near ambient temperature ranges and utilizes relatively large samples which can be highly representative of the end item.
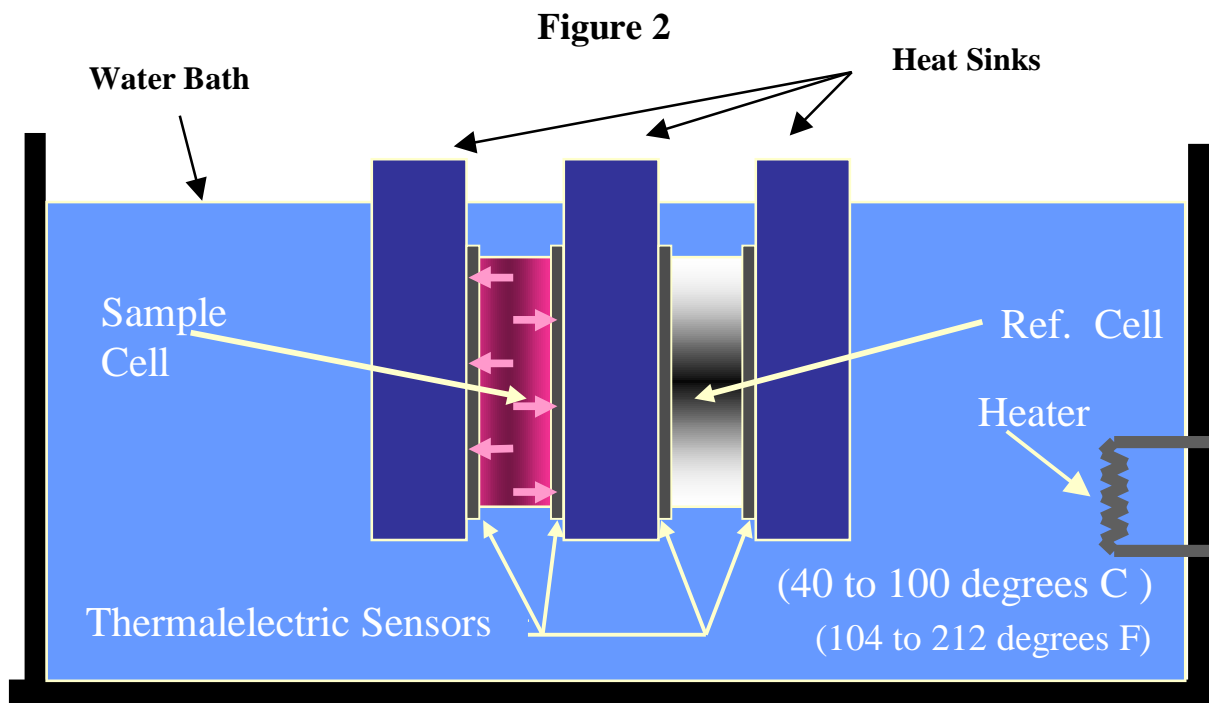
Figure 2

Figure 2 is a simplistic representation of the inner workings of a Heat Flow Calorimeter. The most obvious attribute of the calorimeter is the very large water bath which is held at a constant (+ / - 0.001 degrees) temperature.   Suspended in this bath there is a multi-section heat sink, a number of thermalelectric sensors and two sample cells.   One cell,

referred to as the reference cell, is identical to the sample cell except it contains nothing. Obviously, the sample cell contains the energetic material that is being evaluated. Since all energetic material generates / releases heat as a by-product of the aging process, this additional heat is transferred through the thermalelectric sensors which produce a voltage in proportion to the amount of heat released. By comparing the voltage produced by the two sets of sensors, an extremely accurate determination of the material reaction rate can be accomplished.

The output of the microcalorimeter is used for two very different objectives:

1. To determine how long the material will remain chemically stable.

2. To solve the Arrhenius equation and establish the activation energy of the test material.

These two objectives are the lynch pins to the Predictive Surveillance program. Without this information no real predictive service life program for energetic material is possible.

Once completed, the Kinetics portion of the Predictive Surveillance program provides a prodigious amount of information. This data establishes how rapidly the material ages, how it changes chemically, how long it can be expected to remain chemically stable, and the rate of reaction heat at ambient temperature levels and a measure of the rate of degradation per year. Until the advent of the Heat Flow Calorimeter, there was no method which was capable of measuring all of the degradation products in the 40 to 100 degrees C temperature ranges. By measuring reaction heat at low temperatures, the calculation of the Arrhenius equation is far more meaningful for normal ambient conditions. Once this hurdle was breached, the establishment of an accurate accelerated aging scheme became relatively simple.

The Aging Program - Since the primary aging mechanism for almost all modern ordnance items is storage temperature, the actual process of aging is extremely simple, i.e., raise the temperature above ambient levels and ---- you accelerate the aging process. The trick is knowing what temperature to use and how long to expose the material.

Because of the cost of actually conducting the aging as well as the costs associated with testing, the typical Predictive Surveillance program will restrain this process to one or two accelerated ages. In most cases this means a portion of the test sample will be aged to 10 years and another portion to 20 years. Obviously, there are an infinite number of temperatures that can be used for accelerating the aging process. It would be nice to say that the temperature selected was based on some highly quantifiable and/or scientific basis. The reality is that the temperature used is based on two very non-scientific reasons; 1) the amount of time available to conduct the total program (usually well less than one year) and 2) the most important of all reasons --- available funding.

In the case of small caliber gun ammunition, all the samples are gathered from the same box. Care is taken to assure that any box of ammo selected for evaluation still has the factory seal,

assuring that all of the rounds in that box have experienced the same environmental exposure. Individual rounds are removed, randomly numbered, and then randomly selected for aging or non-aging.   The actual aging is done in a standard T&H chamber and all of the rounds are placed in an aluminum holding fixture which assures uniform heating.

NOTE:

Currently one of the primary assumptions of the Predictive Surveillance process is that while there will be production lot-to-lot variance, the fundamental aging processes are applicable to the entire stockpile.   This assumption will be held as factual until statistically proven invalid.

The Safety / Performance Test Element - It is essential to understand that prior to initiating any safety or performance testing, a large portion of the test sample will be aged to predetermined ages.   By having the same identical energetic material tested at three different ages, a true age-to-performance degradation rate can be established.

The safety and performance testing for gun ammunition is a rather straightforward process.   The tests conducted during the lot acceptance testing are also used as standard for surveillance testing.   These tests include: 1) case mouth pressure, 2) action time, 3) projectile velocity, 4) tracer operation and 5) projectile function.

EXAMPLE OUTCOME

One of the best examples of how the Predictive Surveillance process functions can be observed from the evaluation of 20 mm gun ammunition conducted over the last two years. Since these items are fundamentally pure energetic items without substantial mechanical or electronic components, the Predictive Surveillance processes were recommended to and approved by the Item Manager.   Table 1 provides an example of the type of kinetic data produced by the Predictive Surveillance evaluation of small caliber gun ammunition.

Table 1

Lot No.	Initial Stabilizer Content (%)	Activation Energy (Ea) (Kcal/mole)	Estimated Safe Service Life (in years)			
			77°F	95°F	113°F	122°F
OL85G001-007	0.44	30.262	40.4	7.7	1.6	0.8
OL89K022-007	0.53	30.915	69.7	12.8	2.6	1.2
OL92C025-001	0.54	28.107	43.6	9.4	2.2	1.1
LC92L000E-001	0.57	31.730	66.9	11.7	2.3	1.1
OL93H005-014	0.62	29.948	67.8	13.2	3.0	1.3
LC96L216-001	0.67	28.778	46.2	9.6	2.2	1.1

From a casual perusal of the information provided above, a number of very significant concepts are clear:

1. **Keep your propellant cool.** By looking at the column of data under the 77°F heading, we see that we can expect the gun propellant to remain chemically stable for at least 40 years. This should not be construed as indicating that the propellant will perform satisfactorily for that same period of time, only that it will be chemically stable. If we next look at the 122°F column, we will see that the expected stable life has been reduced to approximately one year. While we have always known that temperature dramatically affects the service life of propellant, this information, presented in this finite manner, brings this concept home to the Item Logistic Manager.

2. **Optimized Stockpile Utilization is possible.** When the kinetics data is provided in a clear and understandable manner, the non-scientific manager is able to comprehend and utilize the information to optimize stockpile utilization. The Predictive process is the key to providing the manager with this required information. In other words, move those lots having the shortest potential service life to those locations where the most training occurs. In this fashion the ammunition would be expended well before the end of service life. This will reduce / eliminate demil actions and assure long term quality assets for the war reserve inventory.

As previously stated, the attribute of chemical stability is not the only significant characteristic which must be addressed by any service life program. Safety and performance testing provides

the true proof of process. Table 2 provides a synopsis of the performance data gathered in the last evaluation.

Table 2

Lot No.	Action Time (4.0 ms max.)			Case Mouth (60,500 psi max.)		
	0 yr.	10 yr.	20 yr.	0 yr.	10 yr.	20 yr.
1	2.75	2.60	2.70	55,500	52,800	52,800
2	2.60	2.50	2.55	52,000	51,400	53,500
3	2.45	2.35	2.40	57,800	59, 600	61,500
4	2.60	2.55	2.55	54,100	51,800	52,300

Lot No.	Velocity (3460 max. & 3360 min.)			Tracer operation		
	0 yr.	10 yr.	20 yr.	0 yr.	10 yr.	20 yr.
1	3,390	3,380	3,375	NA	NA	NA
2	3,380	3,375	3,385	91%	94%	94%
3	3,410	3,425	3,435	100%	94%	94%
4	3,370	3,340	3,340	100%	93%	100%

Shaded area indicates a value out of specification limits.

From a casual glance at the Table 2 data, it is obvious that all data from the un-aged portions of the lots functioned within specifications. If a program were based on monitoring of stabilizer levels and baseline (un-age) functional firing, the inevitable conclusion would have to be that the lots were all satisfactory. Since there are hundreds of ammo lots in the inventory, it is doubtful that any of these lots would ever again be scheduled for service life evaluation. As a consequence, it is highly likely that lot # 3 of Table 2 would at some point in the future, cause significant problems for the Fleet. This is based on the fact that approximately one-half of the rounds aged to 20 years could not be removed from the barrel with the manual extractor. The only way to remove these expended rounds was to use a long ramrod and mallet to drive the case out of the barrel. If these rounds had been fired in a rotary barrel gun, the resulting damage to the gun would have been substantial. In the case of an airborne gun, both the aircraft and pilot would be endangered.

It should be obvious from the preceding data that gun ammunition is one commodity that cannot be evaluated by stockpile sampling. Additionally, the traditional monitoring of the propellant via the fume test does not begin to provide the information required to manage the modern ammunition stockpiles.

CONCLUSION

In this age of Acquisition reform, weapon programs should seriously consider integrating into their acquisition strategy a kinetics based surveillance program. This program would be applicable to all of the weapon energetic components and should at a minimum include the following elements:

      1. Defines the chemical degradation process of the energetic material under evaluation.

      2. Determines the length of time the material will remain chemically stable.

      3. Develops a precision accelerated aging program based on the kinetic data and a 25ºC (77ºF) baseline temperature.

      4. Accelerates the age of a portion of the sample units to a minimum of 20 years.

      5. Conduct safety and functional testing to validate acceptable performance at both zero age and 20 years into the future – as a minimum.

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